

Application of Inverse Iteration to 2-Dimensional Master Equations

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ABSTRACT: Recent developments in unimolecular theory have placed great emphasis on the role played by angular momentum in determining the details of the dependence of the rate coefficient on pressure and temperature. The natural way to investigate these dependencies is through the master equation formulation, where the rate coefficient is recovered as the eigenvalue of the smallest magnitude of the spatial operator. Except for very simple cases, the master equation must be solved with numerical methods. For the 2-dimensional master equation this leads to large sparse matrices and correspondingly lengthy computational times in order to determine the eigenvalue of the least magnitude. A reformulation of the problem in terms of a diffusion equation approximates the final matrix with a narrow banded matrix that can easily be factored using a variation of Gaussian elimination. The 2-dimensional master equation can then be solved with inverse iteration, which rapidly converges to the desired eigenpair. This method can be up to 10 times faster than conventional iterative algorithms for finding the desired eigenpair. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1004–1010, 1997

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Introduction

Statistical theories of unimolecular reactions¹⁻³ have proved very useful in the analysis and understanding of many elementary reactions of importance in atmospheric and combustion systems that often have complex pressure and temperature dependences. The master equation has been particularly useful in this respect.^{1,3} In a typical formulation the total internal energy, E , of the molecule is treated as a stochastic variable and the equation of motion of the probability density of E is expressed as a master equation (ME). The rate coefficient is then the eigenvalue of the least magnitude of the resulting set of coupled differential equations.

The internal energy is not the only constant of motion defining the microcanonical rate coefficient for dissociation. The overall angular momentum, J , is also conserved and thus the state of the unimolecular substrate is more precisely defined by specifying both E and J . Detailed calculations over the last decade have made microcanonical rate coefficients, $k(E, J)$, available for a number of important elementary reactions.⁴⁻¹¹ It is straightforward to introduce the dependence of the microcanonical rate coefficient on J into the ME formalism, and the resulting equation of motion of the joint probability density, $\rho(E, J; t)$, is,

$$\frac{\partial \rho(E, J; t)}{\partial t} = \omega \int P(E, J | E', J') \rho(E', J'; t) dE' dJ' - \omega \rho(E, J; t) - k(E, J) \rho(E, J; t), \quad (1)$$

where ω is the collision frequency and the kernel $P(E, J | E', J')$ is the transition density for collisional transfer from state (E', J') to state (E, J) .

The spatial operator on the right-hand side of eq. (1) is linear and a solution can be expressed by expanding $\rho(E, J; t)$ in terms of the eigenfunctions, $\phi_i(E, J)$, of the spatial operator:

$$\rho(E, J; t) = \sum_i c_i \phi_i(E, J) e^{\lambda_i t}, \quad (2)$$

where λ_i is the eigenvalue corresponding to the eigenfunction $\phi_i(E, J)$ and the c_i are constants that depend on the initial distribution of the system. For unimolecular systems the λ_i are all negative

and for systems with a significant threshold and at moderate temperatures it is also found that the eigenvalue of smallest magnitude, λ_1 , is well separated from the other eigenvalues, often by one or more orders of magnitude. Thus, at long times, times which correspond to the time scales over which experimental measurements are made, the decay of the system is governed solely by λ_1 and it is a straightforward matter to show that the canonical rate coefficient for unimolecular decay can be equated with $|\lambda_1|$.

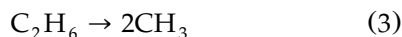
The problem of rate coefficient determination therefore becomes one of determining the eigenvalue of the least magnitude of the spatial operator in eq. (1). The nature of the operator is such that numerical solution is mandatory. The most common approach is to divide the axes of the spatial variables into contiguous intervals or grains^{1,3} to produce a lattice that spans the state space. Each lattice point is assigned a set of mean properties: an average value of each variable (E, J), the number of states associated with these average values, and an average value of the microcanonical rate coefficient. The probability density $\rho(E, J; t)$ is now represented by a time-dependent vector, the elements of which give the probability of the system being found at a particular lattice point. The integral operator is replaced by a matrix that describes the transition probabilities when going from one lattice point to another. The rate coefficient is approximated by the eigenvalue of the smallest magnitude of the matrix representing the spatial operator.

The principal difficulty with this approach is that the size of the matrices generated is generally very large: if 200 grains are used to span the E dimension and 30 grains are used to span J , then a matrix of 6000 squared will result, the diagonalization of which is impractical except on the largest of machines because of the memory requirements. One of the attractive features of MEs written only in terms of E is that they can be manipulated on relatively low CPU power workstations, which has made it possible to analyze experimental data on a routine basis. It is desirable to find methods that allow MEs written in terms of E and J to be treated on machines with similar power. In a recent article Robertson et al.¹² described an approach based on transforming the integral operator of eq. (1) into an equivalent diffusion operator. The resulting diffusion equation (DE) is much easier to handle numerically and results in a sparse banded matrix. Because this problem is negative definite, a

variant of Gaussian elimination without pivoting can be used because it will be stable and will run to completion. Thus, the coefficient matrix can be factored at low cost without a significant increase in the number of nonzero elements that must be stored, and inverse iteration can be used to find the desired eigenpair. The purpose of this article is to report on our successes in the implementation of this method.

The main objective is to develop a method that will give good approximate rate coefficients and associated eigenvectors in a short time, which might form the basis of a more sophisticated iterative method. Iterative methods are computationally demanding, but the resources required can be significantly reduced if an initial estimate close to the actual solution is employed and if a good approximation to the inverse of the matrix is available.

A brief summary of the transformation of the integral operator into a diffusion operator is given, and an account of the factorization and inverse iteration routines for the matrix approximation of the diffusion operator are shown. Results for the reaction,



are also presented.

Diffusion Equation Approximation

The details of the transformation of the integral operator to a diffusion operator have been given elsewhere,¹³ so only a summary will be given here.

Before any solution to the ME equation can be attempted ω , $P(E, J | E', J')$, and $k(E, J)$ have to be defined. ω is taken to be the Lennard-Jones collision frequency.¹⁴ $k(E, J)$ can be calculated by a number of methods, although currently the most tractable are those developed by Smith and Diau,⁶⁻⁸ which are based on the flexible transition state (FTST) approach of Wardlaw and Marcus.^{4,5} The kernel $P(E, J | E', J')$ presents a problem, because little is known of its form and experimental and theoretical approaches to the problem are still in their infancy. In order to make progress a heuristic model has to be adopted that might sensibly be supposed to represent the properties of a real kernel. In MEs written in E only, one of the most extensively used models is the so-called exponential down model¹⁵ (also referred to as the

exponential gap model¹⁶):

$$P(E | E') = A(E') \exp(-\alpha(E' - E)) \quad \text{for } E' > E, \quad (4)$$

where $\alpha = 1/\langle \Delta E \rangle_d$, $\langle \Delta E \rangle_d$ being the average energy transferred in a deactivating collision. This model embraces the notion that collisions that transfer large amounts of energy are less likely than those that transfer small amounts of energy. Such a model could be applied to the total energy part $P(E, J | E', J')$, but this leaves the question of J transfer still open.

A common approximation is to rewrite eq. (1) in terms of rotational and vibrational energies,¹⁷⁻²⁰ E_r and E_v , respectively. The basis of this transform is the rigid rotor harmonic oscillator approximation. Jeffrey et al.²¹ discussed the difficulties with the straightforward application of this transform, especially in connection with detailed balance; but because our goal is to construct an approximate solution, and a starting point for more elaborate iterative techniques, the separation will be adopted here. For a spherical top it allows the total energy to be written as

$$E = E_v + E_r(J) = E_v + BJ(J + 1). \quad (5)$$

The kernel can then be rewritten in terms of these new variables,

$$P(E, J | E', J') \rightarrow P(\mathbf{E} | \mathbf{E}'), \quad (6)$$

where $\mathbf{E} = (E_r, E_v)$ and \mathbf{E}' is similarly defined. The advantage of this transformation is that if motion in the two coordinates can be separated in some sense, then exponential down models can be applied to each energy separately. The most obvious and popular way of separating the kernel is to write it as the product of two 1-dimensional kernels,

$$P(\mathbf{E} | \mathbf{E}') = P(E_v | E'_v) P(E_r | E'_r). \quad (7)$$

An alternative separation, suggested by Oppenheim et al.²² and adopted by Robertson et al.,^{12,20} is the so-called uncorrelated dynamics approximation that can be written as

$$P(\mathbf{E} | \mathbf{E}') = P(E_v | E'_v) \delta(E_r - E'_r) + P(E_r | E'_r) \delta(E_v - E'_v). \quad (8)$$

Roughly speaking this model represents the case where, on collision, either the rotational or the vibrational energy changes but not both at the same time. The substitution of (8) into (1) leads to

splitting of the spatial operator into two operators, one for each energy coordinate, and eq. (1) can be rewritten as

$$\frac{\partial \rho(\mathbf{E}, t)}{\partial t} = \omega L_r \rho(\mathbf{E}, t) + \omega L_v \rho(\mathbf{E}, t) - k(\mathbf{E}) \rho(\mathbf{E}, t), \quad (9)$$

where $\rho(\mathbf{E}, t)$ is the probability density of state \mathbf{E} , L_v is the operator governing motion along the vibrational coordinate, and L_r is the operator governing motion along the rotational coordinate.

The benefit of this approach emerges when the nature of the state space spanned by each coordinate is considered. The relative sparsity of rotational states (the density of rotational states for a polyatomic in the classical approximation goes as $E_r^{1/2}$) means that a continuum approximation (e.g., a diffusion equation) may not be appropriate for this coordinate. Accordingly, an ME based on the individual rotational states gives a better representation of the motion in this coordinate. If the states are numerous and close in energy, graining techniques may be necessary and for heavy systems continuum techniques may become appropriate. For energy ranges that are significant in thermal experiments, 40 rotational grains are usually adequate.

For a relatively large molecule (five atoms or more) the vibrational state densities are large, especially in the region of the threshold, and a continuum approximation is acceptable. Here the drift-determined diffusion approximation described by Green et al.¹³ can be employed. The basis of this approximation is the Kramers–Moyal²³ expansion of the operator L_v ,

$$L_v \rho(\mathbf{E}, t) = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n}{\partial E_v^n} (a_n(E_v) \rho(\mathbf{E}, t)), \quad (10)$$

where

$$a_n(E_v) = \omega \int_0^{\infty} (E_v - E'_v)^n P(E'_v | E_v) dE'_v. \quad (11)$$

The expansion given in eq. (10) is most often truncated at the second term to give a diffusion operator. The a_1 coefficient determines the drift of the population density to equilibrium and is usually denoted μ ; the a_2 coefficient determines the width of the distribution and is usually denoted as σ^2 , or in terms of the related diffusion coefficient, $D = \sigma^2/2$. The disadvantage of this truncation is that the equilibrium solution to the diffusion oper-

ator may no longer be the Boltzmann distribution. This defect may be rectified if the diffusion coefficient is altered so that the equilibrium distribution is Boltzmann by redefining the diffusion coefficient in terms of the drift,

$$D(E_v) = \frac{1}{f(E_v)} \int_0^{E_v} \mu(z) f(z) dz, \quad (12)$$

where $f(E_v)$ is the Boltzmann distribution. Numerical representation of this operator yields a tridiagonal matrix that is much more compact than the original ME.

The combination of the representation of these two operators within the uncorrelated dynamics approximation is shown schematically in Figure 1. The rotational operator is replicated at intervals down the leading diagonal of the matrix and the vibrational transitions are superimposed upon these rotational transitions. The main advantage of the uncorrelated dynamics approximation can now be seen, in that all the nonzero elements are close to the leading diagonal. Thus, the matrix has a narrow banded form and routines specifically designed for this form can be employed. The problem can be further simplified by using detailed balance to symmetrize each coordinate separately, thereby giving an overall symmetric matrix.

Rayleigh Quotient Iteration

In this problem the lowest eigenvalue and associated eigenvector are desired, thus inverse iteration combined with estimates of the eigenvalue with the Rayleigh quotient (i.e., Rayleigh quotient iteration, RQI) is the method of choice. In mathematical terms the method is described by iteration with the following equations until convergence:

$$\mathbf{y} = (\mathbf{A} - \lambda_i)^{-1} \mathbf{x}_i, \quad (13)$$

$$\lambda_{i+1} = \lambda_i + 1/\mathbf{x}_i^T \mathbf{y}, \quad (14)$$

$$\mathbf{x}_{i+1} = \mathbf{y}/\mathbf{y}^T \mathbf{y}, \quad (15)$$

where \mathbf{A} is the ME matrix (or an approximation to it), λ_i is the current estimate of the eigenvalue of interest, \mathbf{x}_i is the corresponding eigenvector estimate, and \mathbf{y} is the unnormalized revised estimate of the eigenvector.

The matrix that results from the diffusion approximation is large, with a bandwidth determined by the number of rotational states. Because the number of rotational states is small in relation

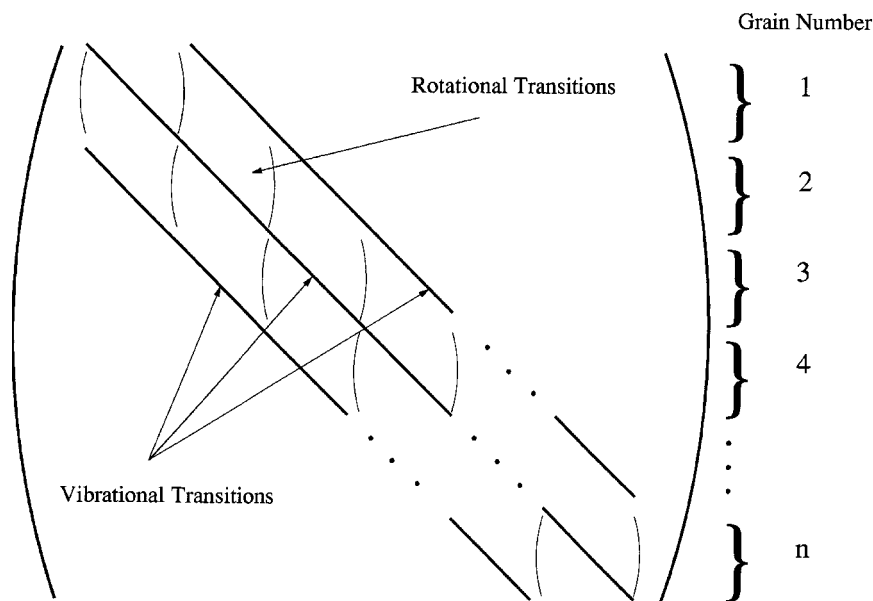


FIGURE 1. A schematic representation of the matrix obtained by combining an ME representation of the rotational operator L_r and the vibrational operator L_v .

to the total number of states, the matrix can be considered to be a narrow banded matrix. In addition, because the matrix is negative definite, a variation of Gaussian elimination without pivoting can be used to explicitly factor the matrix at a cost related to the square of the bandwidth and the size of the matrix. This cost is only slightly more than the cost of a matrix vector multiplication. A benefit of this factorization is that λ_i and \mathbf{x}_{i+1} can be *exactly* calculated, leading to the cubic convergence of the Rayleigh quotient method. This method will converge with only a few iterations, much less than a method based on an approximation to \mathbf{A} .

The particular variant of Gaussian elimination used was the \mathbf{LDL}^T factorization.²⁴ This variant takes advantage of the symmetry of the ME matrix. It is important to note that because the lowest eigenvalue is desired and because this eigenvalue can be very close to zero, a shift can be calculated such that the shifted matrix is no longer negative definite. This fact prohibits the use of the Cholesky decomposition because it involves taking the square root of an element of \mathbf{D} , which may be negative. Because the rounding errors produced in the factorization will in fact aid in the calculation of the eigenvector, we are safe in using the \mathbf{LDL}^T decomposition without pivoting.

The initial estimate of the eigenvector is important, and in this work this initial choice was based

on the strong collision population appropriately modified by the symmetry constraint imposed by detailed balance. The initial guess at the eigenvalue is likewise obtained from the strong collision model, the rate coefficient being recovered as the absolute value of the converged value of λ .

Results and Conclusions

The approach to finding the desired eigenpair outlined in the previous section was tested by calculating the canonical rate coefficient for reaction (3) for a series of pressures and temperatures and comparing results and computer times with those obtained using the Nesbet algorithm.²⁵ The microcanonical rate coefficients used are those calculated by Wardlaw and Marcus using the FTST approach.^{4,5} Values of the sum of states at the transition state, $W(E, J)$, were supplied at a number of different E and J lattice points and a spline interpolation was used to calculate values at the desired points. The density of states of the molecule at equilibrium were calculated on the basis of rigid rotor harmonic oscillator dynamics. Although this approximation will be acceptable for low energies, anharmonic and Coriolis couplings at higher energies will inevitably mean that this approximation becomes less acceptable. A new method recently

emerged²⁶ for computing quantum spectral densities in anharmonically coupled molecular systems, which overcomes this approximation. However, the approximation does have the advantage of allowing a separation of rotational and vibrational energies, which is necessary for the application of the uncorrelated dynamics model. The vibrational coordinate was split into 250 grains of width 200 cm^{-1} and the rotational coordinate was split into 30 grains, each grain containing the states of five consecutive J values. The exponential down model was used as the basis for describing energy transfer in both coordinates. The $\langle \Delta E \rangle_d$ parameter for each coordinate was given the value of 270 cm^{-1} . The bath gas used for the purpose of these calculations is argon and the Lennard-Jones parameters for argon/ethane collisions were taken to be $\sigma = 3.93\text{ \AA}$ and $\varepsilon/k = 163\text{ K}$.²⁷

A further approximation that has been introduced to enhance the speed of calculation is the reduced matrix approximation described by Robertson et al.²⁸ The basis of this approximation is that at low energies far from the threshold, the states can be assumed, to a good approximation, to be in a Boltzmann distribution and that these states have relatively little influence on the overall reaction. It is those states that are closest to the reaction threshold that are the most important in determining the rate coefficient. As a consequence the L_v operator was defined for these states alone with the effect of considerably reducing the size of the matrix that was required.

Table I shows a comparison between rate coefficients obtained using the two different diagonalization routines for a temperature of 600 K. As can be seen the agreement is acceptable. The main difference between the two methods is that the Nesbet based code¹ took over an hour of CPU time while that based on the RQI with exact (LDL^T) factorization to compute the inverse took a mere 28 s on a SunSPARC station 10. The excessive time taken by the Nesbet based code in practice would not be required because only enough iterations would be required to converge the result to within experimental error. The code was allowed to run on in this instance to show that both routines produced the same rate coefficients. Jeffrey et al.²¹ noted that at elevated temperatures the Nesbet calculation is significantly less efficient. To test the efficiency of the RQI algorithm a calculation was performed at 1500 K and a bath concentration of $10^{15}\text{ molecules cm}^{-3}$. Approximate agreement between the two algorithms was achieved after the

TABLE I. Comparison of Rate Coefficients, k/s^{-1} , at 600 K for Dissociation of C_2H_6 Calculated from Nesbet and Inverse Iteration Algorithms.

Concentration/ Molecule (cm^{-3})	Nesbet	Inverse Iteration
0.1×10^7	0.989495×10^{-21}	0.988642×10^{-21}
0.1×10^8	0.984771×10^{-20}	0.983919×10^{-20}
0.1×10^9	0.950987×10^{-19}	0.950149×10^{-19}
0.1×10^{10}	0.861148×10^{-18}	0.860366×10^{-18}
0.1×10^{11}	0.765507×10^{-17}	0.764845×10^{-17}
0.1×10^{12}	0.680610×10^{-16}	0.680055×10^{-16}
0.1×10^{13}	0.585381×10^{-15}	0.584911×10^{-15}
0.1×10^{14}	0.450559×10^{-14}	0.450188×10^{-14}
0.1×10^{15}	0.276281×10^{-13}	0.276048×10^{-13}
0.1×10^{16}	0.127073×10^{-12}	0.126965×10^{-12}
0.1×10^{17}	0.401745×10^{-12}	0.401389×10^{-12}
0.1×10^{18}	0.814058×10^{-12}	0.813272×10^{-12}
0.1×10^{19}	0.111311×10^{-11}	0.111211×10^{-11}
0.1×10^{20}	0.121427×10^{-11}	0.121284×10^{-11}
0.1×10^{21}	0.123194×10^{-11}	0.123063×10^{-11}

Nesbet algorithm had executed 1000 iterations. The timings for the two algorithms were 809 s for the Nesbet algorithm and 4 s for the LDL^T algorithm.

In conclusion the LDL^T algorithm combined with a diffusion approximation for the internal energy modes allows the robust and rapid estimates of the canonical rate coefficient for unimolecular dissociation to be obtained for those systems where angular momentum considerations are important. The intention is to use this method as a preconditioner to enhance more elaborate and accurate iterative methods. This will be the subject of future publications.

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References

1. R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions*, Blackwell, Oxford, 1990.

2. W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York, 1973.
3. K. A. Holbrook, M. J. Pilling, and S. H. Robertson, *Unimolecular Reactions*, Wiley, New York, 1996.
4. D. M. Wardlaw and R. A. Marcus, *J. Phys. Chem.*, **90**, 5383 (1986).
5. D. M. Wardlaw and R. A. Marcus, *J. Chem. Phys.*, **83**, 3462 (1985).
6. S. C. Smith, *J. Phys. Chem.*, **97**, 7034 (1993).
7. E. W.-G. Diau and S. C. Smith, *J. Phys. Chem.*, to appear.
8. S. C. Smith, *J. Chem. Phys.*, **95**, 3403 (1991).
9. S. J. Klippenstein, A. L. L. East, and W. D. Allen, *J. Chem. Phys.*, **101**, 9198 (1994).
10. S. J. Klippenstein, *J. Phys. Chem.*, **98**, 11459 (1994).
11. S. J. Klippenstein, *J. Chem. Phys.*, **101**, 1996 (1994).
12. S. H. Robertson, N. J. B. Green, and M. J. Pilling, *Mol. Phys.*, **89**, 1531 (1996).
13. N. J. B. Green, S. H. Robertson, and M. J. Pilling, *J. Chem. Phys.*, **100**, 5259 (1994).
14. P. D. Neufeld, A. R. Janzen, and R. A. Aziz, *J. Chem. Phys.*, **57**, 1100 (1972).
15. A. P. Penner and W. Forst, *J. Chem. Phys.*, **67**, 5296 (1977).
16. J. N. Murrell and S. D. Bosanac, *Introduction to the Theory of Atomic and Molecular Collisions*, Wiley, New York, 1989.
17. J. Troe, *J. Chem. Phys.*, **66**, 4745 (1977).
18. S. C. Smith and R. G. Gilbert, *Int. J. Chem. Kinet.*, **20**, 307 (1988).
19. S. C. Smith and R. G. Gilbert, *Int. J. Chem. Kinet.*, **20**, 979 (1988).
20. S. H. Robertson, A. I. Shushin, and D. M. Wardlaw, *J. Chem. Phys.*, **98**, 8673 (1993).
21. S. J. Jeffrey, K. E. Gates, and S. C. Smith, *J. Phys. Chem.*, **100**, 7090 (1996).
22. I. Oppenheim, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.*, **46**, 4100 (1967).
23. J. E. Moyal, *J. R. Statist. Soc. (B)*, **11**, 150 (1949).
24. G. H. Golub and C. F. van Loan, *Matrix Computations*, The Johns Hopkins University Press, Baltimore, MD, 1983.
25. R. Nesbet, *J. Chem. Phys.*, **43**, 311 (1965).
26. S. J. Jeffrey and S. C. Smith, *J. Chem. Phys.*, to appear.
27. H. Hippler, J. Troe, and H. J. Wendelken, *J. Chem. Phys.*, **78**, 6709 (1983).
28. S. H. Robertson, M. J. Pilling, D. L. Baulch, and N. J. B. Green, *J. Phys. Chem.*, **99**, 13452 (1995).